

Chapter 10

Lithium-Ion Battery Systems and Technology

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Glossary

Active material	The material in the electrodes of a cell or battery that takes part in the electrochemical reactions of charge or discharge.
Battery/battery pack	An assembly of any number of Li-ion cells, associated electronics, battery packaging, and connector(s).
Capacity	The total number of Ampere-hours (Ah) that can be withdrawn from a fully charged cell or battery under specified conditions of discharge.
Cell	Basic lithium ion unit providing a source of electrical energy by direct conversion of chemical energy that consists of electrodes, separator, electrolyte, container, and terminals, and that is designed to be charged electrically.
Current collector	An inert member of high electrical conductivity used to conduct current from or to an electrode during discharge or charge.
Cycle	The discharge and subsequent or preceding charge of a Li-ion cell or battery such that it is restored to its original conditions.
Cycle life	The number of cycles under specified conditions which are available from a Li-ion cell or battery before it fails to meet specified criteria as to performance.
Electrolyte	The medium which provides the ion transport mechanism between the positive and negative electrodes of a cell.

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Negative electrode	The electrode acting as an anode when a cell or battery is discharging.
Overcharge	The forcing of a current through a Li-ion cell or battery pack after it has been fully charged.
Positive electrode	The electrode acting as a cathode when a cell or battery is discharging.
Separator	An ionically conductive, electronically insulative material which prevents electronic contact between electrodes of opposite polarity in the same cell.
Thermal runaway	The cell condition where the internal cell reactions generate more thermal heat than the cell can dissipate. The condition causes cell venting and premature failure.

Definition of the Subject

Lithium-ion battery (LIB) is one of rechargeable battery types in which lithium ions move from the negative electrode (anode) to the positive electrode (cathode) during discharge, and back when charging. It is the most popular choice for consumer electronics applications mainly due to high-energy density, longer cycle and shelf life, and no memory effect. With Li-ion batteries currently gaining much attraction in electric drive vehicle, the concern for global warming and a clean environment may be well served with advances in such systems.

Introduction

During the last 15 years, lithium-ion batteries have dominated the advanced energy sources by powering the modern portable electronics and replaced many other commercial battery systems in the market. The prime reasons for its rapid success and proliferation in consumer electronic market are its superior characteristics over other battery systems, namely, high voltage, high-energy density, and longer cycle and shelf life with no memory effect. The significant progress of Li-ion batteries is mainly due to numerous innovations and advancements in materials, designs, and safety. This entry is intended to provide an overview of Li-ion batteries on several aspects. Starting with a brief discussion on its history, commercial success, and working mechanism, all the critical components inside the cell have been discussed in adequate detail. The later part of this chapter will primarily focus on manufacturing process, recent advances, and modern trends in Li-ion systems and detailed discussion on Li-ion cell safety.

History of Li-Ion Batteries

The working mechanism of Li-ion cells is often related to that of a rocking chair since within the cell, the lithium ions swing between the negative electrode and the positive electrode through an organic liquid electrolyte, like a rocking chair from side to side. This “rocking-chair” concept was first proposed by M.S. Whittingham at Exxon in 1970s where he discovered the concept of intercalation electrodes using titanium(II) sulfide as the cathode and lithium metal as the anode [1]. The principal concept is based on the intercalation reaction and is rather different from other conventional secondary batteries which are based on chemical reactions.

Goodenough was the first to patent LiCoO_2 as a lithium intercalation cathode material in 1980 [2] and H. Ikeda of Sanyo was the first to patent an intercalation material in an organic solvent such as graphite in 1981 [3]. S. Basu of Bell Laboratories filed an US patent in 1982, based on his finding of lithium intercalation in graphite at room temperature [4]. I. Kuribayashi and A. Yoshino developed a new cell design using an intercalation carbon anode and a LiCoO_2 cathode and filed patents worldwide [5]. In 1991, Sony Energytec Inc. began to produce commercial lithium-ion cells under the leadership of Yoshio Nishi. Bellcore team under the leadership of J. M. Tarascon pioneered the modern concept of “polymer” (soft pack) Li-ion cells [6–9].

Soon after commercialization, the Li-ion battery (LIB) system became a popular choice because of its high-energy density, good performance, and no memory effect as occurred with nickel-cadmium (Ni-Cd) or nickel-metal hydride (Ni-MH) batteries. LIBs have been primarily used for portable electronics, especially cellular phones and notebook computers. Recently, the application area has been extended to power tools, electric bikes, and energy storage systems. Several companies are now working toward adapting the lithium-ion system for use in electric drive vehicle (EDV) applications.

Li-ion cells are being built in many different shapes and configurations—button, flat, rectangular (also referred as prismatic), and cylindrical. The cell components (electrodes, electrolyte, and separator) are designed to accommodate a particular cell shape and design. The separators are either stacked between the electrodes or wound together with electrodes to form jellyrolls, as shown in Fig. 10.1. Typical safety features included in cells with metal enclosure are the PTC and CID devices that are usually incorporated into the cell top plate and seal. The PTC is a positive temperature coefficient device that changes resistance at a set temperature or current flow and stops a thermal runaway condition from developing. The CID is a current interrupt device that is incorporated into the cell cap, and it interrupts the electrical connection between the cathode tab and the positive terminal when the internal pressure in the cell reaches a given pressure. Another safety feature present in Li-ion cell is the cell vent which activates at pressures just higher than the CID to release the volatile solvent and stops cell action.

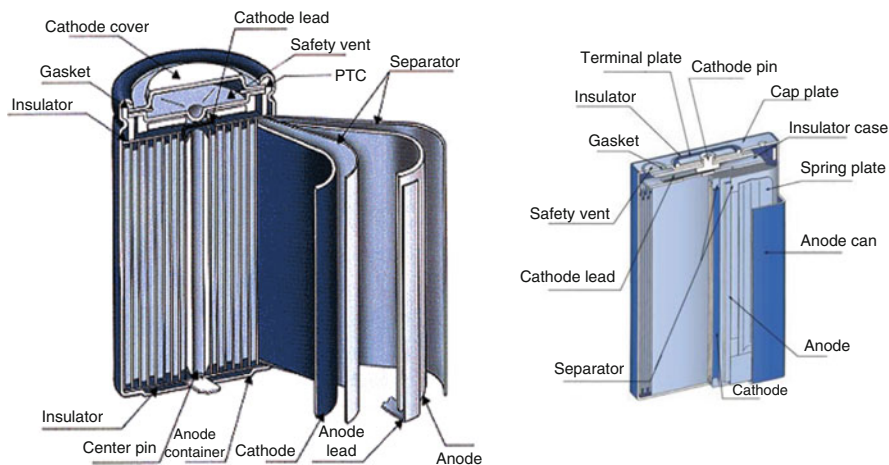


Fig. 10.1 Typical Li-ion battery configuration: (a) spirally wound cylindrical cell, (b) wound type prismatic cell

Commercial Success

The battery industry has seen enormous growth over the past 15 years in portable, rechargeable battery packs. The majority of this surge can be attributed to the widespread use of cell phones, laptop computers, tablet PCs, video games, and other wireless electronics. At present, this technology is gaining worldwide attention as a battery option for transportation applications, including electric drive vehicles namely HEVs, PHEVs, and BEVs.

The higher volumetric and gravimetric energy storage capability are key characteristics of the Li-ion battery system compared to the conventional sealed nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), and valve-regulated lead acid (VRLA) battery systems. Figure 10.2 presents the energy density and specific energy comparisons of small sealed rechargeable battery systems. Some of the distinct advantages of Li-ion system over other commercial rechargeable systems are the choice of chemistry with highest energy and lightest weight, good cycle life, no memory effect, higher energy efficiency, and better high rate capability. Of course there are also certain issues for Li-ion system similar to any other high-energy storage devices that include higher charging times, thermal runaway concerns, relatively more expensive, and requiring advanced protection circuitry for safety and to prevent overcharge and over discharge.

Based on a recent report on rechargeable battery markets that Global Industry Analysts (GIA) announced, the global market for rechargeable batteries is forecast to reach US\$16.4 billion by the year 2015 [10]. Factors driving the market growth include growing consumer acceptance of rechargeable battery technologies in various parts of the world, rapid growth in the electronics market, and increasing role of rechargeable batteries in the automotive sector. It should be noted that in 2006, the

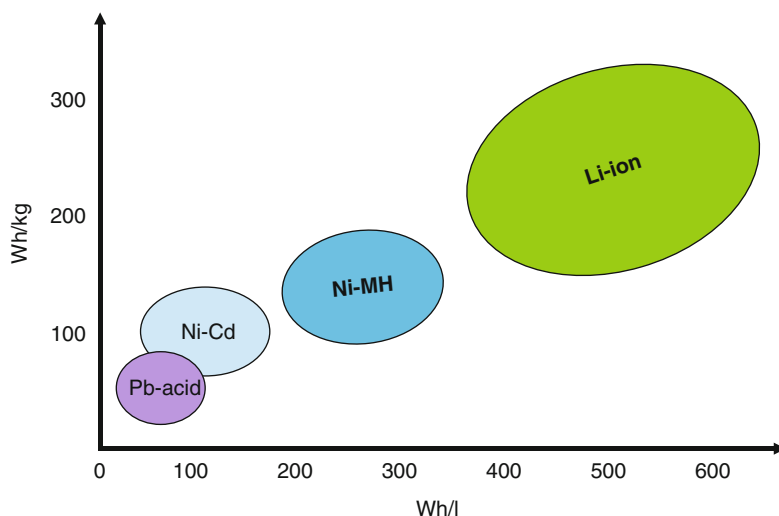


Fig. 10.2 Volumetric energy density (Wh/l) and gravimetric energy density (Wh/kg) for major rechargeable battery systems

market size of rechargeable battery systems for portable power applications was around US\$6 billion out of which Li-ion comprises 75% of the market.

The market survey reports show that the lithium-ion battery is becoming an almighty rechargeable system and in 2010, a whopping sum of around 3.9 billion cells has been supplied all together by cell manufacturers around the world which is about twofold increase in supply compared to 2006 [11] and the supply is expected to grow by at least 15% during 2011. There is a steady increase in the demand for lithium-ion batteries for all portable electronic devices (almost 100% of cell phones and notebook PCs), and in addition, the Li-ion system also started penetrating more and more in other arenas like power tools, energy storage systems (ESS), and so on. Li-ion system now starts competing with Pb-acid systems in the energy storage systems arena primarily due to its superior cycle life and higher columbic efficiency. For the automotive applications, lithium-ion cells have become a hot topic and are now on the verge of being brought on board vehicles on a massive scale. Although the Li-ion battery for HEV application still has little experience in the real market, research and development activity for it is very dynamic at present world-wide. This fact must surely reflect the common recognition that the technology is one of the most promising for the HEV battery of the coming generation. It is predicted that the HEV will be significantly widespread by 2015 and is expected to take a certain portion of the application market at that time.

The tremendous progress in Li-ion cells is clearly visible with as much as a twofold increase in the volumetric and gravimetric energy density combined with a 50% reduction in price was achieved between 1995 and 2006. Figure 10.3 depicts the increase in capacity of the cylindrical 18650 cell (18 mm in diameter and 65.0 mm long) from 1992 to 2006. In 1995, an 18650 cell with a capacity of

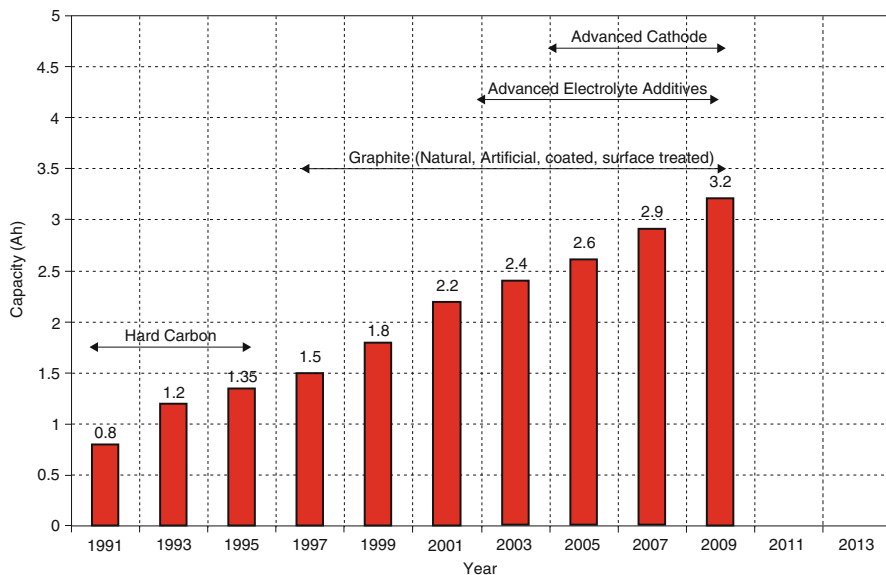


Fig. 10.3 Capacity (Ah) increase for 18650 lithium-ion cell resulting from advances in active materials and functional additives to electrolyte

around 1.5 Ah was sold for \$8, while in 2006, the same size cell with 2.6 Ah sold for about \$4. The early LIBs had a capacity of 800 mAh and an end-of-charge voltage of 4.1 V. The initial cells used hard-carbon anode materials which had a capacity of about 200 mAh/g, and the LiCoO_2 had a capacity of nearly 110 mAh/g due to 4.1 V charging voltage. In 2003, the capacity of the 18650 cell reached 2.4 Ah. This corresponds to an energy density of over 200 Wh/kg or 500 Wh/L, respectively. These values were reached in part by increasing the cell-operating voltage higher than 4.2 V due to the availability of improved graphite anode materials, electrolyte additives, and a stabilized LiCoO_2 .

The cell producers accomplished the performance improvements through engineering improvements in cell design, new electrode materials, and automated high-speed production to reduce the cost. The capacity of the 18650 cell had reached 2.9 Ah in 2007 based on treated graphite anode and planar-nickel-based cathode and with several kinds of electrolyte additives [12]. With further continuous improvements in all the cell components that includes silicon alloy-type anode materials, lithium-nickel-cobalt-aluminum and nickel-manganese-cobalt cathode materials, novel electrolyte and/or additives, some cell manufacturers are currently able to achieve a maximum capacity of up to 3.4 Ah for the same 18650 cell design.

The major Li-ion cell manufacturers are from Japan, China, and S. Korea. [Figure 10.4](#) presents the global market share for bare cell shipment volumes from the three countries cell manufacturers for the consumer portable power applications in 2010. Some of the major cell manufacturers include Sanyo, Sony, and Panasonic from Japan; Samsung SDI and LGChem from Korea; and BYD, ATL, and Lishen from China.

Fig. 10.4 Major cell manufacturers and their lithium-ion battery movement globally in 2010

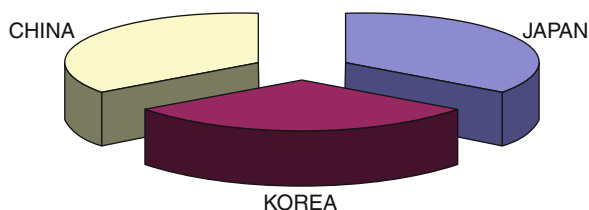


Fig. 10.5 Movements in cell shipment volumes for each lithium-ion battery application globally in 2010

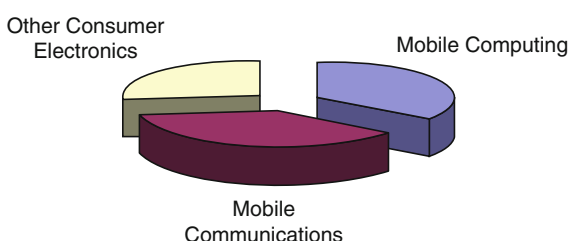


Figure 10.5 shows the split-up of small format LIBs supplied for portable power applications namely mobile computing, mobile communications, and other consumer electronics including power tools during 2010. The thin, rectangular polymer/laminate cell construction has been found increasingly favorable in the modern portable consumer electronics market (e.g., Iphone, Ipad smart phones, and so on). Overall, for the consumer electronics market sector, Japan and Korea dominates the production of 18650 type cells and China dominates in prismatic type cell production. There are no major Li-ion manufacturers in the United States or in Europe, even though they constitute large markets for devices powered by Li-ion batteries [13]. Production activity in the United States so far is limited to companies that supply the niche medical and military markets.

There are many emerging market opportunities for Li-ion cells in transportation. Li-ion batteries can provide very high power and are therefore a good candidate for EDV applications. The automotive power market is viewed as the largest future growth opportunity for Li-ion batteries. Their high voltage, low weight, small volume, and potentially long life make them very attractive. Different cell designs and geometries are currently being adapted by cell manufacturers for automotive applications. A few common designs include rectangular flat pouch cell and larger cylindrical cell design.

The cell's capacities for EDV applications are in the range of 25–100 Ah. The typical energy requirement for plug-in hybrid electric vehicle (PHEV) is between 5 and 20 kWh and for all electric vehicle (EV), the energy requirement is more than 20 kWh with a voltage of 300 V or more. A number of modules with energy in the range of 1–2 kWh are necessary. The advantage of Li-ion over Ni-MH for hybrid electric vehicle (HEV) applications that has an energy requirement in the range of 3–5 kWh is still quite not clear, but with decreasing cost as production volume increases, Li-ion cells are considered to be economically competitive. Once Li-ion system finds its place, the transportation market could dominate over the present portable device market.

Principle Behind Li-Ion Batteries

Lithium-Ion Cell

The primary functional components of a typical Li-ion cell are negative electrode (or anode), positive electrode (or cathode), and electrolyte. Most commonly used negative electrode materials include hard carbon, graphitic carbon, and treated graphite. Typical positive electrode materials may include a layered oxide (lithium cobalt oxide, lithium nickel oxide), spinel (like lithium manganese oxide), or a polyanion (such as lithium iron phosphate). The electrolyte in general contains lithium-containing salt such as lithium hexafluorophosphate, lithium tetrafluoroborate, etc. dissolved in a solvent that comprises a mixture of organic carbonates such as ethylene carbonate, diethyl carbonate, etc. Depending upon the material choice, the cell voltage, capacity, performance, and safety can change dramatically. The most common cell design formats of Li-ion cells include cylindrical, prismatic, and pouch. In this section, the working mechanism of Li-ion cells has been discussed along with an overview of each cell component (negative electrode, positive electrode, electrolyte, and separator). Later part of this chapter would add more information on each of them including the modern trend.

Li-ion Cell Mechanism

A typical Li-ion cell consists of a positive electrode composed of a thin layer of powdered metal oxide (e.g., LiCoO_2) coated on aluminum foil and a negative electrode formed from a thin layer of powdered graphite, mounted on a copper foil. The two electrodes are separated by a porous polyolefin film called as separator soaked typically in a electrolyte made of LiPF_6 salt dissolved in a mixture of organic solvents such as ethylene carbonate (EC), ethyl methyl carbonate (EMC), or diethyl carbonate (DEC).

During cell operation, all the three functional components participate in the electrochemical reaction. Both the negative and positive electrodes are materials into which, and from which, lithium can migrate. During insertion (or intercalation), lithium moves into the electrode and during extraction (or deintercalation), lithium moves back out. During discharge, the lithium ions are deintercalated from the negative electrode moved through the electrolyte and intercalated into the positive electrode. The reverse happens during charging in which lithium ions deintercalate from positive electrode and gets intercalated into the negative electrode. [Figure 10.6](#) shows the schematic representation of the operation of a lithium-ion cell during discharge process. Useful work can only be extracted if electrons flow through a closed external circuit.

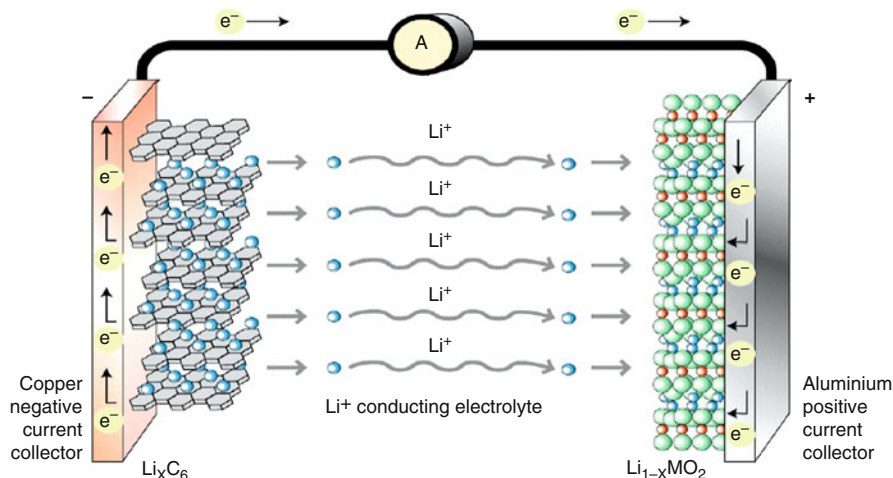
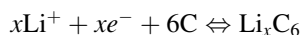


Fig. 10.6 Schematic representation of Li-ion cell operating mechanism

The positive electrode half-cell reaction (with charging being forward) can be represented as:



The negative electrode half-reaction (with charging being forward) is:



where x refer to moles of lithium. The overall cell reaction can thus be represented as:



where the forward reaction corresponds to charging and the reverse reaction occurs during discharge.

Negative Electrode Material (Anode)

The basic requirements for a negative electrode material to be used in lithium-ion cell are that the material should have minimal volume expansion and stress associated with it during charge/discharge process, higher electronic conductivity, lower irreversible capacity loss during first charging or intercalation process, stable under wide operating temperature window in a highly reducing environment, and lower specific surface area (typically $2 \text{ m}^2/\text{g}$) for optimal performance and safety.

There are many types of carbonaceous materials being used as negative electrode active material for Li-ion cells. Carbon materials can be broadly classified into amorphous and crystalline. Crystalline or graphitic carbon is a typical layered compound that consists of hexagonal grapheme sheets. Although graphite exists in nature, it can be synthesized artificially by treating a pyrolyzed carbon at high temperatures around 3,000°C.

Amorphous kind carbon includes materials that are heat-treated at lower temperatures of around 1,100–1,300°C and has low crystallinity. They include “soft carbons” (graphitizable carbons) and “hard carbons” (non-graphitizable carbons). In soft carbons, small crystallites are stacked nearly in the same direction, and thereby, subtle diffusion induced upon heating results in graphitization. In contrast, the crystallites of hard carbons do not have such distinct orientation and, hence, are difficult to develop even when heat-treated at high temperatures >3,000°C. Soft carbon material is mostly being used to surface treat the graphite material. The practical materials most widely used in commercial cells include hard carbon, natural graphite, synthetic graphite, and amorphous carbon coated graphite.

Solid Electrolyte Interface (SEI)

During the first charging after cell assembly, a protective film has been formed on the surface of the negative electrode through reductive decomposition of the electrolytic solution [14, 15]. The passivation film often called as solid electrolyte interface (SEI) acts as an interface between the electrode surface and the electrolyte solution and has the properties of a solid electrolyte with high electronic resistivity. Other favorable properties of the SEI include good mechanical stability/flexibility and good adhesion to the anode. In general, SEI film consists of insoluble and partially soluble reduction products of the electrolyte components. Formation of SEI film suppresses further solvent decomposition and plays a beneficial role in improving the safety and cyclability of lithium ion cells. The SEI formation on negative electrodes thus is a prerequisite for their stable charging and discharging; however, it is the primary cause for the irreversible capacity loss during the first charge through consumption of a considerable amount of lithium. The electrolyte often has additives to enhance SEI formation.

Figure 10.7 shows a typical charge/discharge characteristic of graphitic carbon material. The solid line represents the intercalation or charging, and the dotted line shows the deintercalation or discharging. During first intercalation (charging), the potential drops rapidly after subtle retardation at ~0.8 V (vs. Li^+/Li). Most of the Li intercalation and deintercalation takes place at potentials 0.25 V (vs. Li^+/Li), accompanied by three potential plateaus. Charge consumed upon first charging is not fully recovered upon discharging and the capacity that cannot be recovered is called irreversible capacity which is observed for any carbonaceous material due to the formation of a passive film over the surface of electrode referred as solid electrolyte interface (SEI). At the second and subsequent cycles, graphite shows good

Fig. 10.7 Typical charge/discharge characteristics of graphitic carbon material

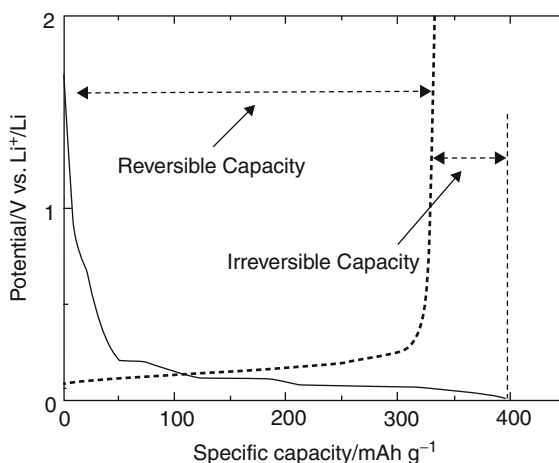


Table 10.1 Properties of few commonly used negative electrode materials for lithium-ion cell

Anode type	First charge capacity (mAh/g)	Irreversible capacity loss	Practical capacity (mAh/g)
Hard carbon	250	25–30%	180–190
Natural graphite	370	16–18%	300–320
Surface treated natural graphite	370	7–9%	340
MCMB graphite	350	10–12%	310–320
Massive artificial graphite (MAG)	360	5–8%	330–340
Mesophase carbon fiber (MCF)	350	10–12%	310

reversibility and the reversible specific capacity ranges from 300 to 370 mAh/g. Table 10.1 shows the properties of a few commonly used negative electrode materials of Li-ion cells. Graphitic carbons can insert lithium up to a stoichiometry of LiC_6 corresponding to 372 mAh/g.

Positive Electrode Material (Cathode)

In general, positive electrodes in commercially available Li-ion cells utilize a lithiated metal oxide as the active material. Most of the research and commercialization efforts has centered on two classes of materials. The first group includes materials with layered structure that enables two-dimensional diffusion of lithium ions or a spinel structure which enables three-dimensional diffusion as the transition-metal ions are ordered in all layers. Examples include LiCoO_2 , LiNiO_2 , $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$, etc. for layered compounds and LiMn_2O_4 for spinel type compound. The second group includes materials with more open structures like vanadium oxide, transition-metal phosphates namely olivine (LiFePO_4). The first group,

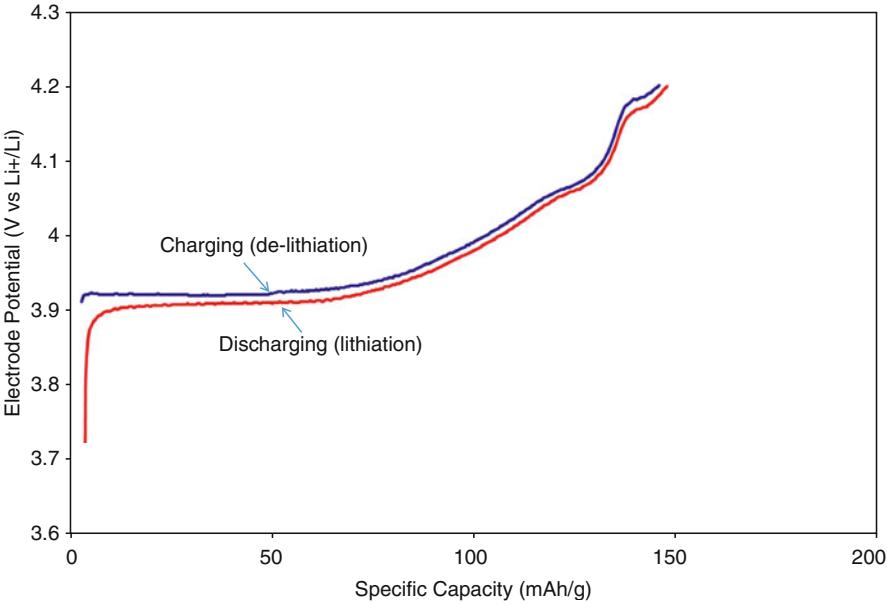


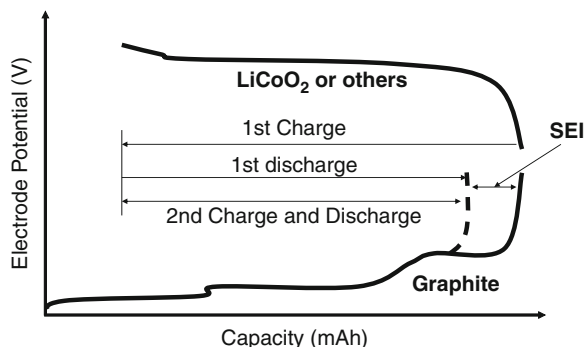
Fig. 10.8 Typical charge/discharge characteristics of lithium cobalt oxide (LiCoO₂) positive electrode material. Charging corresponds to lithium deintercalation, and discharging refers to lithium intercalation

Positive electrode material	Practical capacity for EOCV 4.2 V (mAh/g)	Density (g/cc)
LiCoO ₂	140	5.05
LiNiO ₂	160	4.8
LiNi _{0.8} Co _{0.2} O ₂	140	4.85
LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	160	4.8
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	165	4.7
LiMn ₂ O ₄	100	4.2
LiFePO ₄	120 ^a	3.7

^aCharge cutoff voltage is ~3.65 V

because of their more compact lattices, will have an inherent advantage in energy stored per unit of volume, but the second group compound like LiFePO₄ is cheaper [16]. Figure 10.8 shows the charge/discharge characteristics of LiCoO₂ material. The theoretical specific capacity of the LiCoO₂ cell is relatively low at around 130 mAh/g because only around 0.5 Li/Co can be reversibly cycled without causing cell capacity loss due to changes in the LiCoO₂ structure associated with the phase changes that cause low reaction rates and also poor stability of the electrode at low lithium contents. Table 10.2 shows the properties of a few commonly used positive electrode materials of Li-ion cells.

Fig. 10.9 Schematic showing charge/discharge characteristic of Li-ion cell electrode and state of charge operating window after SEI formation



The ideal requirements for a positive electrode active material used in lithium-ion cell are that the material needs to contain a readily reducible/oxidizable atom, like a transition metal; should react with lithium in a reversible manner without changing the host structure; be a good electronic conductor; be able to react with lithium very rapidly to provide higher power density; should react with lithium with a high free energy of reaction to obtain high voltage, high capacity, and hence high-energy storage; and be stable under wide voltage and temperature window. There are several physical properties that determine the quality of positive electrode active material and also influence the battery characteristics. They include particle size, shape, distribution of particle size, water content, tap density, specific surface area, crystallinity, impurity level, and so on.

Cell Balance

Lithium-ion cells operate by cycling lithium ions between two insertion electrode hosts having different insertion energies. Figure 10.9 shows the schematic of charge discharge characteristics of Li-ion cell electrodes (e.g., LiCoO_2 as positive and graphite as negative electrode) [17]. After assembling and filling with electrolyte, the cell will be in a completely discharged state where all the lithium ions are present in the positive electrode. During initial charging, some portion of the lithium ions goes into the irreversible SEI film formation reaction and rest of the lithium ions gets intercalated into the negative electrode. The negative to positive electrode capacity ratio is very critical in determining the cell performance and safety with continuous cycling. Smaller capacity ratios would present safety hazard as the negative electrode can get overcharged as more lithium ions are available for intercalation than is desirable. Higher capacity ratios may prevent optimal utilization of the negative electrode. The typical negative to positive electrode capacity ratio used by most cell manufacturers is around 1.15. The first charge capacity of negative electrode (Li-ion intercalation) needs to be at least 15% greater than the first charge capacity of the positive electrode (Li-ion deintercalation) to accommodate the SEI formation.

Electrolyte

Electrolyte is one of the critical components for any electrochemical device, and the basic function is to serve as the medium for the transfer of charges, which are in the form of solvated ions, between a pair of electrodes. The role of liquid electrolytes in lithium-ion cells is to act as an ionic conductor to transport solvated lithium ions back and forth between positive and negative electrodes as the cells are charged and discharged. Since the electrodes in lithium-ion cells are the porous composite electrodes, consisting of an active material, a conductive material and a polymer binder, the liquid electrolyte must seep into the porous electrodes and transfer lithium ions smoothly at the interfaces between the liquid and solid phases. The minimal requirements of the electrolyte used in Li-ion cells include good ionic conductivity and electronic insulator property, stability over a wide electrochemical voltage window and operating temperature. Most commonly used salt materials for the electrolyte include LiPF_6 , LiBF_4 , and the most common solvents are carbonate based, namely, EC, DMC, DEC, EMC, and PC.

An ideal electrolyte solvent for Li-ion cells shall meet the following minimal criteria, namely, high dielectric constant, to be able to dissolve salts of sufficient concentration, lower viscosity for facile ion transport, inert to all cell components, especially the charged surfaces of the electrodes, lower melting point, and higher boiling point to remain liquid in a wide temperature range.

An ideal electrolyte solute in lithium-ion cells completely dissolves and dissociate, in the nonaqueous media, and the solvated ions should be able to move in the media with high mobility, should be stable against oxidative decomposition at the positive electrode, should be inert to electrolyte solvents and other cell components, and should be nontoxic and remain stable against thermally induced reactions with electrolyte solvents and other cell components. LiPF_6 is one of the most commonly used salts on commercial Li-ion cells. The success of LiPF_6 was not achieved by any single outstanding property but, rather, by the combination of well-balanced properties, namely, conductivity, ionic mobility, dissociation constant, thermal stability, and electrochemical/chemical stability.

Electrolyte Additives

Electrolyte additives are compounds that add extra functions to the liquid electrolytes in addition to the fundamental function as an ionic conductor. Examples of role-assigned electrolytes include anode passivation film-forming agents, cathode protection agents, overcharge protection agents, wetting agents, flame retardant agents, and so on. It should be noted that small amount of the electrolyte additives dramatically improves the performances of lithium-ion cells. Since the influence of electrolyte additives depends not only on the electrode materials but also on cell designs, the research and development of the additives is quite challenging.

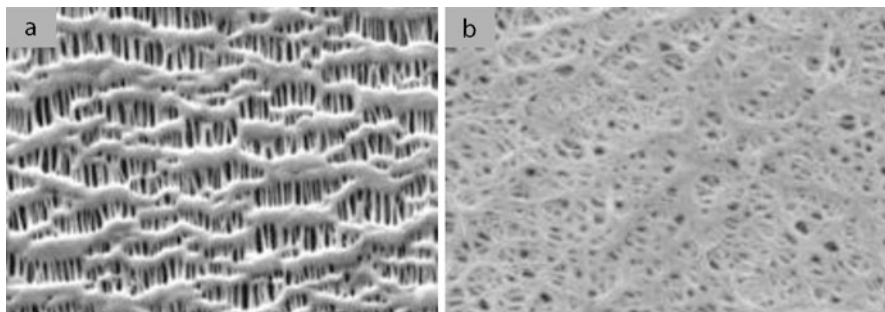


Fig. 10.10 SEM images of separator membrane produced through (a) dry and (b) wet process methods

Separators

A separator is a porous membrane physically placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact between the electrodes. As batteries have become much sophisticated, separator function also has become more demanding and complex. The main function of separator in Li-ion cell is to keep the positive and negative electrodes apart to prevent electrical short circuits and, at the same time, allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell. They should be very good electronic insulators and have the capability of conducting ions by soaking electrolyte. Li-ion battery separators can be produced through dry and wet processes. [Figure 10.10](#) presents the micrographs of separator membrane produced through dry and wet process methods.

A wide variety of properties are required for separators used in Li-ion cells [18]. They include: electronic insulator, minimal electrolyte (ionic) resistance, sufficient mechanical and dimensional stability and physical strength to allow easy handling, chemical stability to degradation by electrolyte, impurities, and electrode reactants and products, readily wetted by electrolyte and effective in preventing migration of particles or soluble species between the two electrodes. In order to achieve good performance of Li-ion cells, the separators should have higher ionic conductivity with electrolyte, low shrinkage, and uniform pore structure. Cells with high-resistance separators will perform poorly during high rate discharge and also will increase the cell-charging time.

Microporous polyolefin membranes in current use are thin (30 μm) and are made of polyethylene (PE), polypropylene (PP), or laminates of polyethylene and polypropylene. They are made up of polyolefin materials because they provide excellent mechanical properties, chemical stability, and acceptable cost. They have been found to be compatible with the cell chemistry and can be cycled for several hundred cycles without significant degradation in chemical or physical properties.

Manufacturing Process

The basic principles and processes of cell design and fabrication are well known and quite similar among cell manufacturers. The International Electrotechnical Commission (IEC) has established a common nomenclature for describing the various cell sizes and chemistry. For example, the most common cylindrical Li-ion cell ICR18650 translates into: I is for Li-ion technology, C for cobalt-based cathode, R is for a round cell, 18 is for the cell diameter in millimeters, and 650 is for the cell height in tenths of a millimeter.

The overall manufacturing process for the Li-ion cell can be divided into the five major processes:

1. Mixing, kneading, coating, pressing, and slitting processes of the positive electrode and negative electrode materials
2. Winding process of the positive electrode, negative electrode, and separator
3. Insertion of the wound cell core and electrolyte injection into the battery case
4. Cell closing or sealing process
5. Formation, aging, and cell selection

Electrode Fabrication and Winding Process

Figure 10.11 shows an outline of the initial process of Li-ion cell manufacturing that includes electrode preparation to winding [19]. In this process, the active materials are coated onto metal foils and calendered for thickness. The positive electrode material consists of active material, such as LiCoO_2 , LiNiO_2 , or LiMn_2O_4 ; a carbon-conductive additive like acetylene black; and a binder material namely polyvinylidene difluoride (PVdF). The active material and conductive agent are first dried and are then fed into a ball mill or other mixer along with the previously prepared binder solution (e.g., PVDF dissolved in *N*-methyl pyrrolidone), and then thoroughly stirred. The ball mill contains ceramic balls, e.g., glass, zirconia, about 2–3 mm in diameter, to assist in mixing and the mixing condition can strongly influence the performance of the cell.

The process for the negative electrode follows essentially similar to that of the positive electrode but with different materials. Carbon or graphite is used for the negative electrode-active material. PVDF, carboxymethylcellulose (CMC), or styrene butadiene rubber (SBR) is generally used for the binder that is usually dissolved in solutions like NMP depending on the type of binder.

A better result in mixing may be obtained by first kneading the materials into a stiff paste and then adjusting the viscosity by adding the solvent so that it can be applied easily in the coating process. The electrode slurries (viscosity from 10,000 to 20,000 cps) are uniformly coated onto both sides of the current collector (aluminum foil for the positive and copper foil for the negative) of

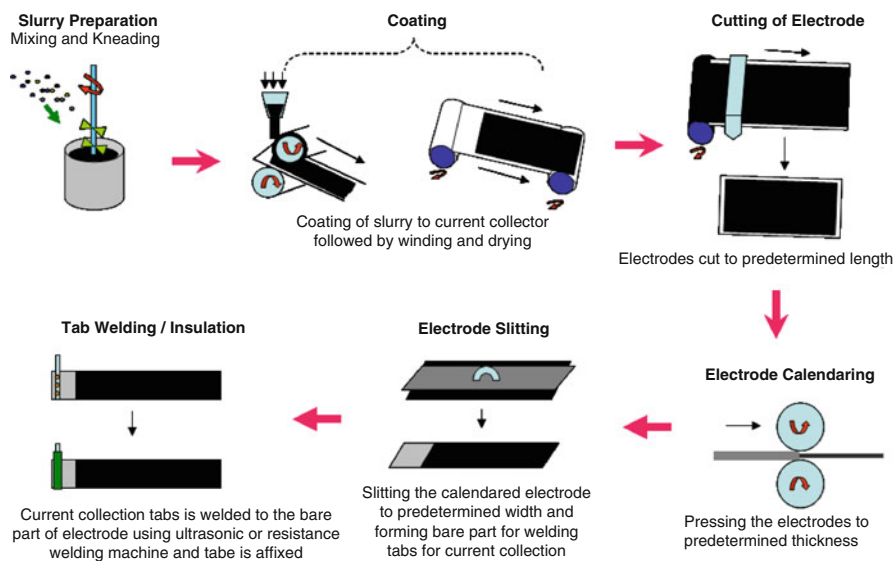


Fig. 10.11 Schematic of battery electrode fabrication process

10–20 μm thickness. Proper mixing techniques are very critical to obtain uniform distribution of the components of the active mass during the coating operation.

Coating operations can use a slot die, reverse roll coating, or doctor blade coating equipment. Close control of coating thickness is essential to ensure that all the parts fit into the can during final assembly. The coating thickness for different cell designs can vary from 50 to 300 μm , depending on the cell design. The coated material is dried in a continuous process. The coating solvent is collected to prevent emission of toxic vapors. Next, the dried electrodes undergo calendaring process where it is compressed with a roller press machine to provide accurate thickness control of the electrode thickness and to increase the density of the electrode mass. After calendaring, the master roll is slit to the width specified for cell construction and wound onto a roll for the winding operations.

18650 Cell Fabrication Process

Figure 10.12 presents the schematic of the assembly of cylindrical cells [19]. The reels of the slit anode, cathode, and separator stock are mounted on the winding machine. The strips have been sized for length, width, and thickness that match the cell design. Once the foils are threaded into the machine, the machine starts and continues to operate automatically until the reels are used up. An aluminum tab is

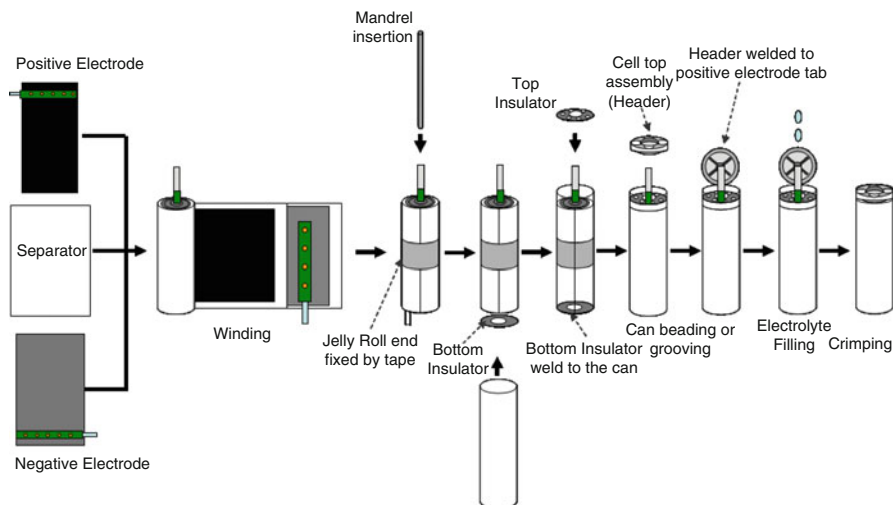


Fig. 10.12 Schematic of 18650 cell fabrication process

affixed to the bare part of the aluminum foil positive electrode by ultrasonic welding before winding, and similarly, a nickel or copper tab is affixed to the copper negative electrode collector by ultrasonic welding.

The winding machine then combines the two electrodes and separator strip on a mandrel (also referred as pin) and winds the combination in jellyroll fashion into a tight bobbin or cell core. Cylindrical cells are wound on a round mandrel while the prismatic cells use a flat paddle. Winding requires constant tension on the coil as it is formed and grows to the final size. Any irregularity leads to a gap between the separator and electrode, resulting in a nonuniform current distribution that can lead to a malfunction or shortened cycle life. The wound coil is checked for internal shorts before being inserted into the can with a hi-pot or impedance tester. In the last step, the cell core is taped to keep it tightly wound before inserting it into the cell case. It is important that the active material neither peels or sloughs off of the active material nor the separator twists during the winding process. Early rejection of potential cell faults is economical and prevents investing more work on bad/faulty cells.

Following insertion into the cell case, a tubular mandrel with a serration may be inserted in the winding core. The function of this mandrel is to improve the integrity of the cell core and for safety of the battery. When the internal pressure rises, gas has free passage through the hollow center of the mandrel and is released through the vent. When the cell is crushed, the mandrel causes both electrodes to short-circuit and instantaneously discharge. Any moisture contamination of the cell has a deleterious effect on its operation. Therefore, all cell assembly operations are usually carried out in a dry room or dry box. Alternatively, the cell then may be put in a heated vacuum oven for certain durations in order to extract residual water from the cell core before electrolyte filling. In the next process, the cell is filled with the electrolyte using a vacuum injection apparatus.

After filling, the cell cap, also called the header, is welded to the aluminum tab and the cell is finally sealed by crimping the header to the can. The header contains the polymer spacer, vent, PTC, and CID safety devices designed to activate and prevent dangerous temperatures and pressures from developing internal to the cell. After sealing, the cells are completely washed with isopropyl alcohol or acetone in order to remove any adhering electrolyte. An electrolyte leakage test is done using a smell sensor apparatus in order to confirm a good seal. Finally, the cell is subjected to an aging process to select out cells with microshorts and to categorize cells by capacity for assembly into battery packs. The temperature, length of storage, and cell checking methodology vary. This process is designed to identify cells with internal cell faults and microshorts that are not found during cell fabrication.

Large Format Li-Ion Cell Manufacturing Process: Flat Plate Pouch Configuration

Li-ion polymer and flat plate cells are produced in small sizes for cellular phones (about 0.5 Ah and higher) and large sizes (up to 200 Ah) for energy storage and motive power applications. A common characteristic is that the polymer separator holds the electrolyte and forms a physical barrier between the anode and cathode to prevent internal shorting. Most polymer cells are flat plate (prismatic) construction.

There is no one general cell fabrication process for polymer, flat or pouch, cells as there is for the liquid electrolyte cylindrical and prismatic cells. Each manufacturer has a slightly different process flow. Cell designs are essentially laminated constructions produced by several different fabrication processes. A typical example was shown in [Fig. 10.13](#) [19]. Cell assembly follows the general outline as that for cylindrical cells. The cell assembly could be either a wound design or a stack design. Wound design follows closely to that of cylindrical cell except that the mandrel would be a thin flat plate depending upon the width requirement. In stack design, positive and negative electrodes along with separator are stacked together to give the desired cell capacity. Alternatively, a Z-fold construction may also be used with the electrodes bonded to the separator [20]. The stacks then are bonded together using ultrasonic or heat to ensure uniform bonding and dimensional control.

The cell case is formed from an aluminum-polymer laminated film. The film is fusion bonded, the electrode stack is inserted, and the exterior case is fused by a heat or an ultrasonic sealing apparatus. The assembly then is checked for internal shorts, the moisture is removed by heating in a vacuum dryer, the electrolyte (polymer or conventional electrolyte depending upon the cell kind) is then injected, and the cell is vacuum-sealed in a two-chamber configuration. After formation, any gas formed is removed by a vacuum, the cell resealed, and the gas chamber discarded. Finally, the cell is subjected to

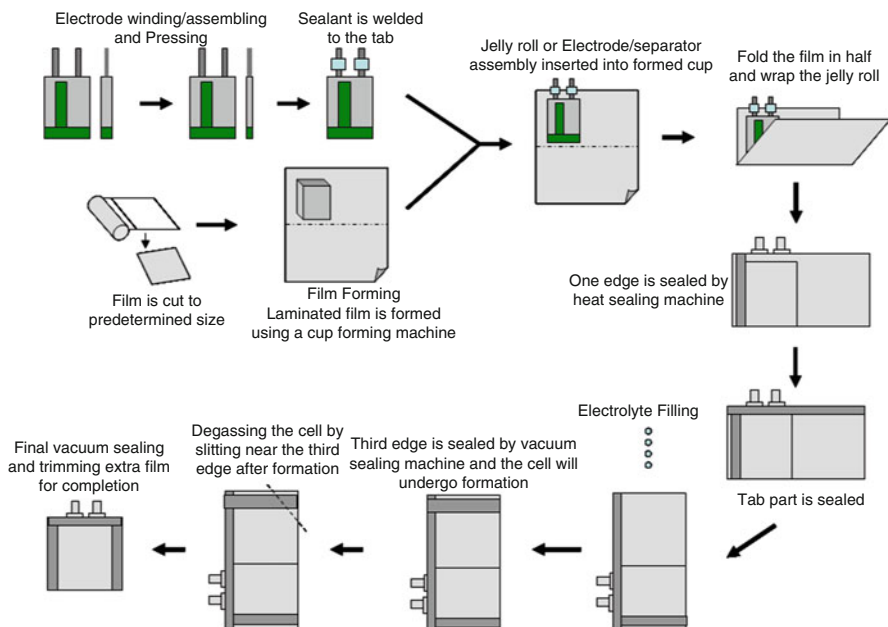


Fig. 10.13 Schematic of pouch cell fabrication process

top sizing, both side bending, leakage tested with an odor sensor, cleaning and drying, inspection of any coil winding misalignment using an X-ray apparatus, lot number printing, storage, charging and discharging, and then final inspection.

Formation and Aging

Once the cell assembly process is complete, the final step in the overall production process shifts to the formation and aging of the cells. This applies to cylindrical, prismatic, flat plate, and polymer cell constructions. Li-ion cells are assembled in the discharged condition and must be activated by charging. The first charge is called “formation,” which activates the active materials in the cells and establishes their ability to function. The first charge typically starts at a lower current to properly form the protective solid electrolyte interface (SEI) layer on the graphite/carbon anode and then increases to the normal current at about 30% into the charge period.

The cell voltage is measured after the first charge and stored (aged) for a set time period. The storage time and temperature vary from one manufacturer to another. The voltage and capacity measurements are stored for use in the cell-selection/-matching process. These will be used later to sort cells out with

internal microshorts or other manufacturing defects. Differences in voltage at the start and end of the storage period can be used to identify problem cells with low voltage and low capacity. Cells with low voltage result from “soft” or “micro” internal shorts and are discarded. The exact first charge regimen and cell-selection procedure may vary with manufacturer. Some manufacturers give the cell one or two cycles after formation to check the capacity for cell matching in assembly of battery packs. Others use the voltage measurement after first charge.

In order to keep up with the market demands, tough quality, performance, and safety requirements, in the cell fabrication methods and process control techniques, are followed. Optical and X-ray systems are currently being used to continuously monitor critical processes like winding, and ensure precise placement of components. The electrolyte-filling process is completely automated by using precision pump combined with advanced multistep vacuum/pressure cycles to ensure that the electrolyte permeates and completely fills the porosity in the separator and electrode structures. The internal construction of every cell produced is inspected by X-ray for proper top cap installation, misalignment of the winding from processing, the improper bending of the tabs, and so forth, which potentially could cause an internal short circuit or cell malfunction.

Safety

Lithium-ion batteries have been commercially available for over 2 decades and currently represent state-of-the-art power source for all modern consumer electronic devices. Due to its advanced chemistry, Li-ion cells exhibit superior performance characteristics over most other rechargeable battery systems. The lithium-ion technology offers a high energy and power density, long life, and reliability that makes it attractive for electric drive vehicle (EDV), military, and aerospace fields, and large format Li-ion cells and battery packs are currently under development for such applications.

Like any other energy storage devices, one of the concerns about the Li-ion technology is the safety associated with the system and is the primary focus for cell/pack manufacturers apart from cost and durability. Li-ion cells can undergo thermal runaway if subjected to unreasonable conditions for which they are not designed as it involves a combination of highly energetic materials with flammable electrolyte solutions.

With several billion Li-ion cells being used to power cell phones, laptops, and other consumer electronics, there are bound to be concerns over field incidents [21–23]. Battery failures that vent with fire are taken very seriously and manufacturers choose a conservative approach by adopting safety recalls. Considering the number of lithium-ion batteries used in the market, this energy storage system has caused little harm in terms of damage and personal injury.

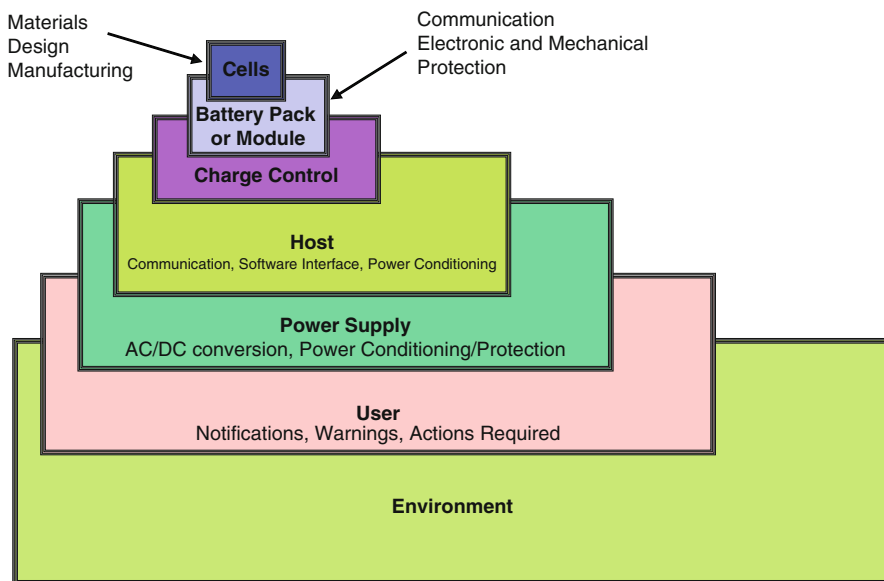


Fig. 10.14 System approach to Li-ion design and use (IEEE)

Li-ion cells have had an excellent safety record in the field with very few documented safety events in over one billion cells in the market place. Safety is continuously improving since production rates are increasing. This excellent safety record has come about due to care on the part of manufacturers and due to regulatory standards like IEEE, IEC, and UL governing the safety of cells. Cell manufacturers are not only trying packing more energy into the pack but also attempting to make it safer. However, there is still room for further improvement in safety as Li-ion system moves into several new arenas like electric cars and trucks, stationary energy storage, military and satellite applications that mostly utilize larger format batteries.

System Level Safety

In general, ensuring a safe product begins at cell level and ends with the user. The IEEE 1625 standard for laptops and the IEEE 1725 standard for mobile phones have recently focused on conveying the concept that Li-ion battery pack safety is a function of the entirety of the cell, pack, system design, and manufacture [24, 25]. A system level approach thus becomes very essential in addressing the safety of Li-ion batteries. System level safety includes the combination of cell, battery pack, host device, power supply, or adapter, end user/environment, and each of these aspects has a role to play in ensuring pack safety. Figure 10.14 presents the schematic of the system approach to Li-ion design

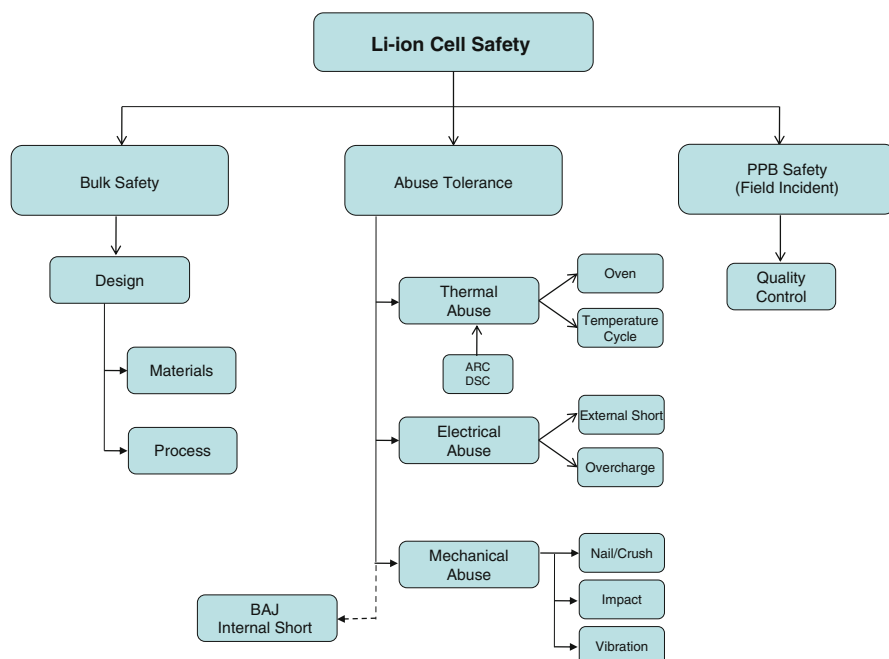


Fig. 10.15 A schematic flowchart that represents the cell level safety in Li-ion cells for consumer electronics applications

and use. The level of assurance for protection and safety on system level depends on the implementation by the manufacturer/supplier and also on the actions of the end user. This part of system level safety is about understanding the intended use of a product, and mitigating reasonable and foreseeable misuse that may occur. IEEE P1625, the Standard for Rechargeable Batteries for Portable Computing, was the first standard to encompass all levels of the battery manufacturing process and include the customer experience.

Cell Level Safety

The safety of lithium-ion batteries is an essential requirement for commercial use. Cell manufacturers continue to work toward designing safer cells, through modifications of cell components and through improvements in manufacturing practices that ultimately resulted in cells exhibiting excellent safety record in the field. On cell level, thermal runaway failures can occur for a number of reasons, including poor cell design (electrochemical or mechanical), cell manufacturing flaws, external abuse of cells, etc.

The cell level safety can be broadly classified into three categories shown in Fig. 10.15. The first one represents safety that depends upon cell design aspects, namely, materials and process conditions. Cell manufacturers around the world are

now adapting more sophisticated processes to produce Li-ion cells. The process is highly automated and more efficient with advanced quality control checks based on optical and X-ray inspection techniques to check on several key safety-related factors such as electrode alignment, presence of metal contaminants, presence of burrs in electrode edges, insulation of aluminum current collector next to electrode coating that faces the negative electrode, and so on. Moreover, using advanced electrodes with surface treated and core-shell type materials, very safe electrode capacity ratio, through implementing several cell level safety features, etc., greatly improves the cell level safety. The category can also be referred as bulk safety as almost 99.999% of the cells produced currently for consumer electronics applications by well-experienced cell manufacturers fall into this category. Bulk safety is not a concern with current advanced Li-ion technology as cells are being made with optimized process conditions, with robust design and advanced material choice that when operated under recommended user conditions is much safer and will not result in thermal runaway situations during its operation period.

The second category addressing cell level safety concern is the abuse tolerance. The term “abuse” refers to using of product in a way that is not intended by the supplier but which may result from unreasonable human behavior or unreasonably extreme environmental conditions [24]. Cell designs that are tolerant to abuse conditions without venting or self-destruction are imperative. Abuse tolerance tests for consumer electronics cells are defined by International Electrotechnical Committee (IEC), Underwriters Laboratories Inc. (UL), and Japan Storage Battery Association (JSBA). The tests are typically classified as thermal, electrical, and mechanical abuse tests. Thermal abuse tests include high-temperature ramp also referred as hot-oven test and temperature cycling test. Characterization test methods, namely, ARC and DSC, are widely used to study the thermal properties of the cell components such as self-heat rate, onset runaway temperature, and so on that are directly linked to the thermal stability of the materials, and these test methods provide insight on thermal abuse tolerance response of Li-ion cells. Overcharge and external short circuit tests are categorized as electrical abuse tests and the most common mechanical abuse tests include crush, nail penetration, crush, impact and vibration tests. For more details regarding each test condition, UL document 1642 could be referred [26]. Cell manufacturers in general adopt a scaling method in quantifying the abuse response of Li-ion cells. The response may be ranging from least severe ones, namely, no change, vent with electrolyte leakage, to the most severe ones like smoke with fire and explosion. For abuse tolerance tests, the criterion for the cell to pass is no fire and no explosion.

The third category is the PPB or parts per billion level safety that refers to the field incidents of Li-ion cells that were subjected to normal recommended operating conditions. Field failures typically represent unprovoked battery explosions, and according to industry experts, such events are rare and it is estimated that one in ten million lithium-ion batteries fail that way [27]. Stringent quality control measures and new safety evaluation methods are being recommended that would help in controlling PPB level. Battery

Association of Japan has developed a test methodology to analyze internal short occurring in a Li-ion cell and to characterize the failure associated with it [24]. With this test method, the field incident caused by internal short circuit can be simulated practically [28]. With the increase in the energy of lithium-ion batteries, more advances in safety technology are also necessary to reduce the field incidents still further and gain more consideration from EDV, satellite, and other specialty applications.

More Details on Cell Components and Modern Trend

Negative Electrode Material

Hard Carbon

One of the typical examples for hard-carbon materials is the thermal decomposition product of polyfurfuryl alcohol resin (PFA). Hard-carbon materials can offer higher capacity beyond the theoretical limit of LiC_6 at lower potentials but have not achieved broad acceptance because of their higher irreversible capacity and sloping discharge voltages [29]. They are highly sensitive to moisture and are difficult to process; however, the material is practically usable and able to offer around 200 mAh/g capacity. Significant research work has been carried out on hard carbon with the purpose of overcoming the drawbacks through surface modifications and pretreatments. But graphitic carbon is still considered the best choice in practical batteries because of its higher performances.

Graphite Intercalation Compounds (GIC)

Theoretically, graphitic carbons can insert lithium up to a stoichiometry of LiC_6 corresponding to 372 mAh/g. The process is called intercalation and Li-ions occupy sites between graphene planes. Morphology of graphitic materials has a strong impact on electrochemical behavior and strongly influences critical stages in the precipitation of the surface films and their passivation properties. In general, graphite particles with some degree of disorder show high reversibility and stability in Li insertion process and are less dependent on solution composition when compared to highly ordered materials.

Graphite intercalation compounds (GIC) have a significant feature called the staging phenomenon, which is characterized by a periodic sequence of intercalant layers (lithium ions) between graphite layers. The n th-stage compound consists of intercalant layers arranged between every n graphite layers. The first-stage lithium graphite intercalation compound has the stoichiometry of LiC_6 with the specific

capacity of 372 mAh/g, a theoretical saturated value of lithium storage for graphite under normal pressure. The staging phenomenon can be easily monitored and controlled by the electrochemical reactions of carbons in Li^+ -containing electrolytes, for instance, conducting galvanostatic (constant current) charge/discharge [30] and slow cyclic voltammetric (CV) [31, 32] tests, and analyzing the differential capacity (dQ/dV vs V , where Q is capacity and V is voltage) has proven to be a particularly useful electrochemical method. In conjunction with the electrochemical techniques, some physical methods have been applied to shed light on the stage occurrence and transitions during lithium intercalation into and deintercalation from graphite host. These methods include in situ XRD [30, 33], ex situ XRD [34], in situ laser Raman spectra [35], and STM [36].

Natural Graphite

Natural graphite is chosen for lithium-ion battery anode materials mainly because of its low cost, low and flat potential profile, high Coulombic efficiency in proper electrolytes, and relatively high reversible capacity (330–350 mAh/g). On the other hand, it has two main shortcomings, namely, low rate capacity and incompatibility with PC-based electrolytes.

The low rate capacity is primarily due to its high anisotropy causing unfavorable orientation of particles that leads to sluggish of Li^+ intercalation and inadequate electronic contact between graphite particles and copper substrate [37, 38]. To overcome this issue, mechanical millings have been applied to pulverize the natural graphite flakes into small pieces [39], through which the preferred orientation of crystallites within each natural graphite flake particle can be distorted to some extent by separated graphite fragments. One other limitation of natural graphite is its incompatibility with PC-based electrolytes. Studies have been carried out to overcome this through modifying the electrolytes with additives and also modifying the graphite by coating amorphous carbon layers through thermal vapor decomposition technique [40–42].

Synthetic Graphite

Synthetic graphite has many properties that are similar to those of natural graphite. Besides, it has many unique merits such as high purity, variety of structures suitable for smooth Li^+ intercalation and diffusion, and so forth. Nevertheless, it is more expensive because of the high-temperature treatment ($>2,800^\circ\text{C}$) on soft carbon precursors, and its reversible capacity is a little smaller than natural graphite.

Graphitized MCMB, mesophase-pitch-based carbon fiber (MCF), and vapor-grown carbon fiber (VGCF) are the representatives of benchmark synthetic graphite anode materials for Li-ion batteries in the market today. Graphitized MCMB has many advantages, namely, high packing density that guarantees high-energy density, and small surface area that decreases the irreversible capacity corresponding to

electrolyte decomposition; most surfaces of MCMB spheres are composed of edge-plane surfaces, thus facilitating Li^+ intercalation and higher rate capability, ease of spreading onto copper foil.

Although amorphous carbon and spherical mesophase base graphite have been used mainly as anode materials in Li-ion cells, artificial graphitic carbon also called as massive artificial graphite (MAG) with lower voltage and the higher energy density is being used mainly to fulfill the difficult requirement for mobile equipment in recent years. MAG has been developed for the mass production of unique graphite for the purpose of battery application [43].

The MAG particles consist of spherical aggregation of fine, flat crystals. It has an average diameter of 20–30 μm and an aspect ratio of about one. MAG particles have a pseudo-isotropic texture where primary flat particles are randomly aggregated that also aids in tolerating expansion and shrinkage during charge/discharge operation. The discharge capacity of MAG exhibits a value of 362 mAh/g, which is very close to the theoretical one (372 mAh/g) of graphite. Graphite with a high crystallinity, which has a smaller interlayer spacing in the crystal, has relatively higher discharge capacity. This could be attributed to the fact that the graphite with the higher crystallinity is mainly composed of regular stacking structure, which is suitable for the formation of Li-GIC. Studies also have shown that the movement of Li^+ ions in MAG occurs in the vertical direction to the collector during the charge/discharge and Li^+ insertion into graphite occurring at the edge of graphite crystal, thereby having an easier lithium transfer and hence better high rate performance compared to flaky natural graphite [43].

Lithium Titanate Anode

Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, referred to as LTO) is another promising anode material for certain niche applications that require high C rates, fast charging capability. Some of the challenges for the LTO-based cells include lower voltage (2.5 V vs. LCO and 1.9 V vs. LFP), lower capacity, and excellent high-temperature stability. It has superior high rate performance with very long cycle life. It is being developed for automotive and energy storage applications.

Silicon-Based Anode

Existing lithium-ion batteries using graphite anodes have inherent limited Ah capacity. Silicon-based anodes theoretically offer as much as a tenfold capacity improvement over graphite. Silicon, when converted to the compound $\text{Li}_{21}\text{Si}_5$ by reaction with lithium in an electrochemical cell, has a maximum capacity of 4,200 mAh/g [44]. Due to its relatively low cost, low toxicity, and higher theoretical capacity, silicon is one of the promising candidates to replace graphite anode in Li-ion systems.

However, implementation of Si as an anode material is greatly hampered by several factors such as large volume change, low intrinsic electrical conductivity, and poor cyclability. The loss of capacity on repeated cycling is attributed to mechanical fragmentation and electrical isolation of silicon species due to the volumetric expansion and contraction associated with lithium insertion and extraction [45]. Many experimental techniques were investigated to analyze the cycling behavior and investigate mechanical degradation upon cycling [46, 47]. The reaction of silicon with lithium produces various alloy-type compounds (Li_xSi_y) and causes enormous volume changes of up to 300% during the charge/discharge process, and this, together with the low electrical conductivity of silicon, obstructs the commercial use of silicon as a negative electrode material [48].

There are several approaches used to date for investigating silicon-based anodes. The thin-film approach involves deposition of an active silicon layer as a continuous media on a specially roughened metal or carbon current collector using ion sputtering [49, 50] or vapor deposition techniques [51, 52]. The film formation method, which results in strong adhesion between the current collector and very thin silicon layer, leads to the formation of a stable, self-organized columnar structure during the first volumetric expansion. This structure remains stable over cycles and aids in providing cycling stability of the films. Despite such attractive features of thin silicon film electrodes, they are yet to be commercialized. The thin silicon film electrodes are an order of magnitude thinner than cathodes, which might cause technological problems [53] and does not seem to be easily scalable. Moreover, solid electrolyte interface (SEI) film formation mechanism has yet to be studied in detail [54] and might highlight potential complications for real LIB employing such electrodes, especially during long-term cycling.

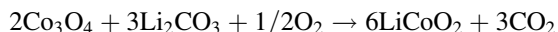
The approach is the composite electrode approach that relies on the use of silicon in the form of tiny silicon “cores,” uniformly distributed within an electrochemically active or inactive buffering media, which prevents silicon-silicon interaction and the formation of large clusters. The core-shell structured anode materials comprising Si/SiO₂ blended with graphite material are good examples for the composite concept and have been gaining much attention primarily due to its ability to deliver higher capacity with continuous cycling, longer and stable cycling performance with much lower volume change than other silicon-based systems under study. Mixtures of silicon and different blends of graphite were studied and it was found that graphite is important in improving cycling performance [55, 56]. To suppress the volume effects of silicon upon cycling, techniques such as pyrolyzed PVC reactions and high-energy mechanical milling (HEMM) were adopted to disperse ultrafine silicon into a feasible carbonaceous matrix that shows promising results on improving the coulombic efficiency after the first cycle [57]. Further optimization of Si-composite based anodes could lead to practical lithium-ion batteries with high-energy density.

Positive Electrode Material

LiCoO₂

Lithium cobalt oxide (LCO) is the primarily used positive electrode–active material of Li-ion rechargeable cells. The simplicity involved in manufacturing and the balanced cell characteristics, namely, cycle performance, rate capability, high and low-temperature performance, safety, and so on, are some of the reasons why LCO is a leading player among positive electrode–active materials. However, as the Li-ion market is driven by cost reduction both in consumer electronics and in the vehicle and stationary storage segment combined with the present higher market price of cobalt, the application of LCO material is decreasing and focus now shifts more toward nickel, manganese, and iron type materials and cobalt-doped layered mixed oxide materials.

LiCoO₂ is obtained using a cobalt compound and a lithium compound as the raw materials and heating. Today cobalt oxide (Co₃O₄) is used as the cobalt compound and lithium carbonate (Li₂CO₃) as the lithium compound due to the stability of their quality and supply, the easiness of handling. The reaction scheme for the LiCoO₂ can be indicated as:



Goodenough recognized that LiCoO₂ had a structure similar to the layered structures of the dichalcogenides and showed that the lithium could be reversibly removed electrochemically, thus making it a viable cathode material [58].

LiNiO₂

Lithium nickel oxide is isostructural with lithium cobalt oxide and has higher specific capacity. However, it is much more susceptible to thermal runaway and has not been used in commercially lithium-ion cells.

LiMn₂O₄ (Spinel)

James Hunter of Eveready Battery Co. was the first to patent spinel cathode material. The application of material to Li-ion system has been developed by J. M. Tarascon [59] and extensively studied by M. Thackeray [60]. Generally, lithium spinel oxides suitable for the cathode are limited to those with a normal spinel in which the lithium ions occupy the tetrahedral (8a) sites and the transition-metal ions reside at the octahedral (16d) sites. Currently, spinel is the center of much interest as the cathode material for large format lithium-ion cell for hybrid electric vehicle applications where high power, safety, and low cost are the strongly required features.

Olivine Compound (LiFePO₄)

A number of researchers have pursued the oxides of iron as potential cathode materials for Li-ion cells. The first cathode material produced in this category is LiFePO₄ [61]. Its low cost and environmentally benign characteristics could have a major impact in electrochemical energy storage. Orthorhombic LiFePO₄ of the olivine structure forms FePO₄ during charging/discharging, and two crystal phases exist during charging/discharging; thus, it exhibits a flat discharge curve with a discharge potential of 3.4 V [62]. The specific capacity of LiFePO₄ is lower compared to nickel and cobalt-based materials. Substitution of iron by manganese transforms the shape of the charge/discharge curves, and this proved effective in increasing the energy density [63, 64]. The capacities of the lower voltage (3.5 V) and higher voltage region (4.0 V) correspond to the content of iron and manganese. Modified LiFePO₄ material too makes it more stable and compatible with a wide range of electrolyte solvents that greatly enhances performance and rate capability.

Mixed Oxide Cathodes

Nickel Cobalt Dioxide, LiNi_{1-y}Co_yO₂, and Nickel Cobalt Aluminum oxide, LiNi_{1-y-z}Co_yAl_zO₂

In general, the introduction of cobalt into nickel oxide structures leads to more stability and nickel oxide structures are less likely to lose oxygen than the pure nickel oxide, and studies on the structural details and physical properties of the mixed oxide system showed that there is an increased ordering with increase in the cobalt concentration. An issue with all these layered oxides is their electronic conductivity, which is not uniformly high across the lithium composition range or nickel substitution. For example, cobalt substitution in LiNiO₂, as in LiNi_{0.8}Co_{0.2}O₂, reduces the electronic conductivity at 4.2 V significantly. These dramatic changes demand that a conductive diluent be added to the cathode-active material, which reduces both the energy storage and the power capabilities.

Substituted nickel oxides, such as LiNi_{1-y-z}Co_yAl_zO₂ (NCA), are prime candidates for the cathode of advanced lithium batteries for use in large-scale systems as required for hybrid electric vehicles. They currently are the battery of choice for satellite applications. On charging these mixed oxides, the nickel is oxidized first to Ni⁴⁺ then the cobalt to Co⁴⁺ [65]. The significant feature of NCA type material is its increased thermal stability by doping with cobalt and aluminum. The temperature of the exothermic peak with oxygen evolution increased from 200°C of LiNiO₂ to 310°C of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ due to the decrease in the nickel content and the aluminum doping [66]. The thermal stability has been considerably improved and there is no oxygen evolution observed below 300°C. Moreover NCA type material has a higher capacity, better cycle life and also rate capability than that of the conventional cobalt-based cathode.

Nickel Cobalt Manganese Oxide, $\text{Ni}_x\text{Co}_y\text{Mn}_z\text{O}_2$

One other commonly used mixed oxide material as positive electrode is cobalt- and manganese-doped lithium nickel oxide. In general, addition of nickel suppresses manganese dissolution to a great extent, thereby enhancing the cycling performance especially at higher temperature. The most common stoichiometry is the 333 compound $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ synthesized using coprecipitation method by Ozhuku et al. [67] and Jeff Dahn in Canada (3 M). There have been many studies on the 333 compound, which have been made by a number of synthetic techniques over a wide range of temperatures. Most of these studies show similar behavior with the capacity of around 165 mAh/g increasing with increasing charging potential [68–70]. The material attracts much attention because of the large battery capacity of about 200 mAh/g, and is a promising material in future. However, the material has certain disadvantages associated with the physical property, namely, lower tap density, smaller particle size that leads to lower energy density and thus mostly preferred to be used in the mixed cathode material. Similar to NCA type material, for the NMC material also, the DSC peak temperature related to the oxygen evolution shifts to the higher temperature as the increase in manganese doping amount and the amount of heat generation decreases extremely. The thermal stability of the cathode material thus could be improved by manganese doping [71].

High-Energy Structured Type and Layered Cathode Materials

There are several approaches currently being pursued to improve the cathode energy density, high rate performance, and cycling performance. One of the means to achieve the trade-off properties, namely, higher capacity and superior thermal stability, is through core-shell structured type electrodes. Higher capacity would be delivered by the core material, and structural/thermal stability would be achieved by the shell material [72–74]. A typical example is NCM type material in core to provide higher capacity surrounded by Ni-/Mn-based layered oxide as shell to offer good thermal stability.

One other approach is a composite layered oxide synthesized through continuous, low-cost highly homogenous coprecipitation process that provides higher capacity and cell voltage. One typical example is $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNiO}_2$ that claims to deliver around 250 mAh/g with longer cycle life and is able to operate at 4.6 V with surface modification [75, 76]. Other approaches include: surface treated cathode like AlF_3 -coated cobalt-doped material to improve cycle life and power when operated at elevated temperatures and pseudo co-crystal-like structure with particle surface doping (e.g., LiCoO_2 type core material with the surface being treated with dopants like magnesium) to improve stability of the structure. Coating the positive electrode with materials such as Al_2O_3 , AlPO_4 , and ZrO_2 is also being actively pursued and used in commercial Li-ion cells [77–79]. Such surface coatings provide superior charge discharge characteristics, increased rate capability, long cycle life, and enhancement in structural stability, and this also elevates thermal stability.

Electrolyte and Additives

For the battery electrolyte, more focus is on developing additives to carry out additional functions to improve the performance and safety also referred as role-assigned electrolytes. Sanyo [80] and Saft [81] companies were the pioneers in proposing Vinylene carbonate (VC) as a solvent additive for graphite based electrochemical systems. VC is one of a popular additive for battery electrolytes typically being used as an anode passivation film-forming agent offering excellent stability and improvement in cycle life. The addition of VC has shifted the decomposition temperature of the SEI to a higher temperature, and this enhanced thermal stability can explain the suppression of the reaction between the electrolyte and the anode when the SEI is broken and repaired. It is considered that the relatively thinner homogeneous SEI formed by VC is an origin of the better cell performances, although the quality of its SEI is strongly dependent on the kind of graphitic carbons and charging conditions.

Sulfite compounds, namely, ethylene sulfite (ES), propylene sulfite (PS), dimethyl sulfite (DMS), and diethyl sulfite (DES), were also being used as passivation film-forming agents especially for PC-based electrolyte, and these compounds were reduced at about 2 V versus Li^+/Li to form the passivation layers, which hindered the PC co-intercalation into the graphene layers [82–84]. Cyclic sulfonate compounds, namely 1,3-propane sulfone (1,3-PS), were reported to give a good SEI film, which resulted in improving cycle and storage performances of cylindrical hard-carbon/ LiMn_2O_4 cells [85].

Some key additive materials used as overcharge protection agents include biphenyl (BP), cyclohexyl benzene (CHB), and hydrogenated *m*-terphenyl (H-mTP). BP polymerizes [86, 87] on the positive electrode during overcharge and the liberated protons migrate to the anode, generating hydrogen gas. This mechanism is used for the overcharge protection: In case of cylindrical cells with pressure-activated current interrupted devices (CID), the internal pressure rise by H_2 evolution helps to operate them and prismatic cells utilize the current shutdown mechanism by the increase in the internal resistance by the polymerized film and the meltdown of polyethylene separators [88].

For protecting the cells from overcharge, one other method is including redox shuttle-type compounds as additives in electrolyte. A compound “R” with a reversible redox potential is added to the electrolyte solution. The R is oxidized to compound “O” on the positive electrode, and then O migrates to the negative electrode and is reduced to the original form R. The requirements for such a compound are that the redox potential should be slightly positive (0.1–0.2 V) to the formal potential of the positive electrode at the end-of-charge and the redox reactions during overcharge should be kinetically reversible on both the electrodes. Some examples include aromatic compounds like 2,4-difluoroanisole (DFA) [87], 4-bromo-1,2-dimethoxybenzene [89], and 2,7-dibromothianthrene [90].

Wetting characteristics are very critical for cell design to obtain optimal performance. In general, one might expect that the solvents and liquid electrolytes will be attractive to hydrophilic surfaces such as cathode materials, but repulsive to

hydrophobic ones such as polyolefin separators and carbonaceous anode materials [91]. The separator wettability can limit the performance of batteries by increasing the separator and cell resistance. The contact angle is a good measure of wettability. The uptake of electrolyte can be enhanced by wetting agents such as methyl phenyl carbonate (MPC) [92] and di-octyl carbonate (DOC) [93].

The additives used in electrolyte as a flame-retarding agents include trimethyl phosphate (TMP), phosphazene derivatives, namely, hexamethoxycyclotriphosphazene (HMPN), tris(2,2,2-trifluoroethyl)phosphate (TFP), and hexamethylphosphoramide (HMPA). Due to the passivation layer formed by these flame-retarding additives [94–96], the exothermic peaks were depressed and also the self-heat rate occurring at elevated temperature thereby provided safety during abuse situations. In addition fluorinated ester group materials (e.g., FEC) are also being used as additive to electrolyte to improve upon high-temperature stability [97–99]. There are also several ongoing research activities on molten salt electrolytes to gain the benefits of the nonflammable characteristics, but overcoming the conductivity issues is still challenging.

Separators

The process for making Li-ion battery separators can be broadly divided into dry and wet processes. Both processes usually employ one or more orientation steps to impart porosity and/or increase tensile strength. Dry process involves melting a polyolefin resin, extruding it into a film, thermal annealing to increase the size and amount of lamella crystallites, and precisely stretching to form tightly ordered micropores. In this process, a row lamellar crystal structure is generated in the polymer in the initial extrusion step. This nonporous structure is highly oriented as a result of extrusion and annealing conditions. In the next step, film is stretched to form micropores. This microporous structure is continuous throughout the bulk interior of the membrane. No solvents are required to produce separator membranes through dry process method.

Wet process also called as phase inversion process involves mixing of hydrocarbon liquid or some other low-molecular-weight substance generally with a polyolefin resin, heating and melting the mixture, extruding the melt into a sheet, orienting the sheet either in the machine direction or biaxially, and then extracting the liquid with a volatile solvent. The structure and properties of the membranes can be changed by controlling the composition of the solutions and the evaporation or subtractions of solvents in the gelation and solidification processes. The separators made by wet process use ultrahigh-molecular-weight polyethylene (UHMWPE). The wet process method is not applicable for polymers such as polypropylene, which do not dissolve in conventional solvents.

Shutdown separators are one of the safety devices inside the cell and act as a last line of defense. The separator shutdown is irreversible, which is fine for

polyethylene-based separators, which melt at around 130°C. The impedance of the separator increases by two to three orders of magnitude due to an increase in cell temperature, which results from cell abuse (e.g., short circuit, overcharge). The separator not only should shut down around 130°C, but it also should maintain its mechanical integrity at higher temperatures. The high-temperature melt integrity of separators also is a very important property to keep the cell safe during extended overcharge or during extended exposure to higher temperatures.

Many technology advancements and improvements are achieved for the separators that also enable the Li-ion cell to operate more reliably under wide ranges of voltage and temperature for prolonged cycles. Separators existing in current market exhibit superior uniformity in thickness and pore distribution, higher strength, and dimensionally more stability at elevated temperatures. The separator membrane shows higher thermal stability through blending with high melting polymer resins. Ceramic material coating on top of polyolefin separator is currently becoming a popular choice for large format Li-ion cells for EDV applications to improve safety. Ceramic layer controls the shrinkage of the separator significantly especially at temperatures close to the melting points of polyolefin, thereby enabling the separator to isolate the electrodes for much higher temperatures.

Battery Management Systems

Owing to the fact that no two cells in a battery are exactly identical, their parameters such as capacity, voltage may vary by a fraction even when manufactured under similar conditions with advanced quality control protocols. In the case of a new battery, these factors may not be very noticeable, but play a major role in determining the performance of the pack with continuous charge/discharge cycles. This problem is easier to detect in a battery of up to 6–12 cells as the case in NBPC battery packs. A faulty cell can be easily disguised in a large battery pack consisting of tens or hundreds of series-connected cells as will be used for EDV applications. Thus, it becomes very essential to monitor the batteries individually and detect faults early.

A battery management unit (BMU) monitors and controls a battery pack. To increase the capacity and voltage, cells are connected in series-parallel arrangements. A typical laptop battery pack would contain a total of six 18650 cells where three cells are connected in series and two of the three cell series combination are connected in parallel. This setup is commonly denoted as 3S2P configuration. In the case of electric vehicle applications, it is common to have several hundred cells in series-parallel arrangements to get the desired voltage of 300–400 V and capacity.

The basic functionalities in a BMU consist of safety functions, voltage and current measuring, state of charge (SOC), and temperature monitoring. For Li-ion battery packs, battery management is the most essential as cells are needed to be controlled individually. When all cells are in parallel, the voltages are forced to be

equal according to Kirchhoff's circuit laws, and hence, no balancing is needed. When the cells are connected in series, the voltages will differ and hence need balancing.

Cells in a battery pack may have slightly different voltages and capacity after complete charge due to minor differences in capacity, impedance, and rate of self-discharge. Cell balancing has been used to reduce the voltage differences among cells, thereby enhancing capacity and cycle life. Overvoltage safety detection functions will abort charging of the battery when any cell reaches its overvoltage threshold. Therefore, other cells may stay undercharged. One consequence is that the battery's full capacity will not be available for discharge. The same occurs when the weakest cell reaches the lower threshold, resulting in capacity not being used. Without balancing, the different cell capacities will start to drift with every charge/discharge cycle, leading to a decrease in the battery pack's total performance.

Cell balancing can be carried out using current bypass by burning up energy through a resistor as heat. This is often referred as passive balancing where to even out differences; the lowest cell determines the level of capacity after balancing. Passive balancing shall not be applied during discharge as it reduces the available capacity of the battery. One other means of balancing is active balancing where energy would be passed from a cell with higher voltage to a cell with lower voltage.

In electric vehicle applications, battery management is essential and much more demanding than for portable batteries. It has to interface with a number of other onboard systems, has to work in real time in rapidly changing charge/discharge conditions as the vehicle accelerates and brakes, and it has to work in harsh and uncontrolled environments. Determining the battery state of charge is particularly critical in electric vehicle applications since these batteries require both high-power charge capability (regenerative braking) and high-power discharge capability for start or acceleration. Therefore, they must be maintained at a SOC that allows delivering the required power, while still having enough "headroom" to accept regenerative charge without overcharging the cells.

In addition to current and voltage monitoring, the BMU also monitors the temperature of the cells in all modes of operation (drive, charge, etc.) and controls the pump, fans, and heater to manage the temperature of the battery. Battery thermal management is critical for the battery life and the vehicle performance, and it is done through the battery electronic control unit. The goal is to make a battery pack work at an optimum average temperature (with life and performance trade-off) with even temperature variations in the modules and within the pack.

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